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(54) Title: SMALL PARTICLE SIZE LATEXES			
(57) Abstract This invention provides certain water-dispersible polyesters which are useful as stabilizers in the preparation of vinyl and acrylic latexes. The polyester/acrylic hybrid latexes so provided have a high solids content and contain markedly reduced levels of coagulum.			

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SMALL PARTICLE SIZE LATEXES

Field of the Invention

5 This invention belongs to the field of polymer chemistry. In particular, it relates to small particle size latexes obtained by emulsion polymerization.

Background of the Invention

10 The particle size of a latex can often have a direct impact on the performance of a coating prepared from that latex. Among those properties that can be affected are gloss, clarity, film formation, and
15 substrate penetration (i.e., for porous substrates). In a very general sense, a smaller particle size will have a positive effect on such properties. Small particle sizes (i.e., < 100nm) are most often achieved by using relatively high levels (2-4 wt%) of small molecule,
20 typically anionic, surfactants such as AEROSOL-OT, sodium dioctyl sulfosuccinate and AEROSOL NPES 2030, ammonium nonylphenoxy polyethoxy ethanol sulfate, which are anionic surfactants sold by Cytec Industries, Inc. However, small particle size and the properties directly
25 affected by it are not, the only important properties in water-based coatings. Of primary importance is the water-resistance/sensitivity of the final film. In small particle size systems, the high level of anionic surfactant, the very component in the latex which gives
30 the small particle size and all of its concomitant advantages, is also likely to be detrimental to water-resistance.

 One further challenge in the preparation of any stable latex is production of a stable emulsion with
35 minimal amounts of coagulum. As noted in Emulsion

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Polymers and Emulsion Polymerization, "The Formation of Coagulum in Emulsion Polymerization", by J.W.

Vanderhoff, 1981, American Chemical Society, coagulum, i.e., polymer recovered in a form other than that of a stable latex, is produced in all sizes of reactors and poses several problems. Such problems include loss of yield of the desired latex, processing difficulties due to the necessity of clean-up, more batch-to-batch variation in latex properties, and health, safety, and environmental problems insofar as the coagulum must be disposed of; this is made more problematic due to entrapment within the coagulum of toxic monomers such as vinyl chloride and acrylonitrile. According to this reference, the formation of coagulum is due to either a failure of the colloidal stability of the latex during or after polymerization, which leads to flocculation of the particles or by polymerization of the monomer(s) by mechanisms other than by the intended emulsion polymerization.

20 U.S. Patent No. 5,342,877 describes a method for preparing small particle size latexes via copolymerization of hydroxyalkyl (meth)acrylates (15-40 weight percent based on total latex solids) and other vinyl/acrylic monomers (particularly styrene) in the presence of water-dispersible polyesters.

25 U.S. Patent No. 4,939,233 describes a method for preparing water-dispersible polyester/vinyl acetate copolymer blends via emulsion polymerization using sulfonated polyesters as stabilizers in the reaction.

30 U.S. Patent Nos. 4,946,932 and 5,277,978 describe a method for preparing water dispersible polyester/-acrylic copolymer blends via emulsion polymerization in the presence of sulfonated polyesters as stabilizers.

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U.S. Patent No. 5,156,651 describes water dispersible polyester/vinyl aromatic latexes for textile sizing applications.

U.S. Patent No. 4,839,413 describes the use of low
5 molecular weight (i.e., less than 20,000) alkali-soluble resins as "support resins" in emulsion polymerization. The support resin is formed via non-aqueous polymerization methods and is subsequently dispersed/dissolved in alkaline solution. The emulsion polymerization is then
10 carried out, at high pH, in the presence of this dissolved support resin and an additional costabilizer (surfactant). A pH of greater than 8 is taught to be necessary.

U.S. Patent No. 5,258,355 describes a dye element
15 for thermosublimation printing comprising a support and a dye acceptor layer containing a graft copolymer of an unsaturated copolyester as the graft base and a vinyl copolymer as the graft shell.

JP 73 102887 describes the emulsion polymerization
20 of vinyl bromide in the presence of catalysts consisting of peroxides and heavy metal salts.

U.S. Patent No. 4,543,401 describes a process for the suspension polymerization of vinyl chloride, in the presence of a redox catalyst system consisting of a
25 peroxyester or diacyl peroxide and isoascorbic acid.

WO 95/01381 describes polymer blends comprising water-dispersible sulfonate group-containing polyester or polyester-amides, styrene polymers, and either a different water-dispersible sulfonate group containing
30 polyester or polyester amide or a nonylphenol ethoxylated surfactant.

WO 95/01399 describes blends of water-dispersible sulfonate group-containing polyester or polyester-amides and styrene polymers.

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Summary of the Invention

This invention provides certain water-dispersible polyesters which are useful in preparing
 5 polyester/acrylic hybrid latexes. The polyesters of the invention are particularly effective stabilizers for vinyl and acrylic latex emulsion preparation, thereby providing emulsions with high solids content without the formation of significant amounts of coagulum. The
 10 latexes of the invention have a particle size of less than 100nm and are useful in coatings compositions, in inks, and in adhesive compositions.

Detailed Description of the Invention

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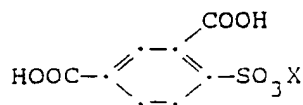
The present invention provides a polyester/acrylic hybrid latex having a particle size diameter of less than about 100nm, prepared by the emulsion polymerization of ethylenically unsaturated monomers in
 20 the presence of a polyester stabilizer, wherein said polyester stabilizer is a water-dispersible polyester comprised of:

- (i) monomer residues of at least one aromatic or
 25 aliphatic dicarboxylic acid;
- (ii) monomer residues of at least one difunctional sulfo monomer selected from the group consisting of

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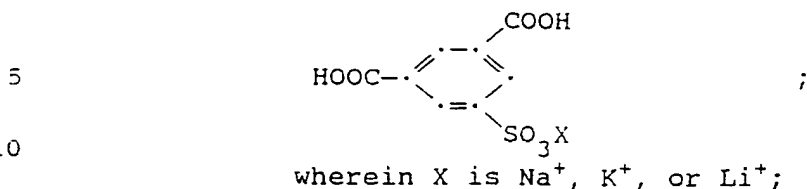
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and

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- 15 (iii) monomer residues of at least one diol or a mixture of a diol and a diamine, wherein said diol is selected from the group consisting of aliphatic and cycloaliphatic glycols; and optionally:
- 20 (iv) monomer residues of at least one difunctional monomer reactant selected from hydroxycarboxylic acids, aminocarboxylic acids and aminoalkanols;
- 25 wherein the weight percent of -SO₃X groups is about 7 to 8%, and the sum of the weight percent of -SO₃X groups and oxygen, excluding the oxygen in said -SO₃X groups, in said polyester is about 30 to 32%.

30 As a further aspect of the invention, there are provided the above water-dispersible polyesters per se. Preferred latexes and polyesters are those in which the weight percentage of -SO₃X groups in the water-dispersible polyesters is between 7.5 and 8. In these

35 ranges, the range is based on the case where X is Na⁺; thus, if X is K⁺ or Li⁺, the ranges will be changed accordingly. The aromatic diacids are preferably selected from the group consisting of terephthalic acid, isophthalic acid, and phthalic acid. The aliphatic

40 diacids are preferably chosen from those having the general formula HOOC-(CH₂)_n-COOH, wherein n is an integer of from 1 to 12, or are selected from the group consisting of 1,2-, 1,3-, and 1,4-

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cyclohexanedicarboxylic acid, maleic acid, fumaric acid, and 5(6)carboxy-4-hexyl-2-cyclohexene-1-octanoic acid.

In the above polyesters, it is preferred that the combination of aromatic diacids and difunctional sulfomonomers comprise about 50 to 100 mole percent of the total dicarboxylic acid moieties. The aliphatic dicarboxylic acids thus comprise the remainder of the dicarboxylic acid moieties. The glycol residues are preferably comprised of residues of one or more ethylene, diethylene, triethylene, tetraethylene, propylene, and dipropylene glycols and cyclohexanedimethanol. It is further preferred that ethylene glycol comprises less than 75 mole % of the total glycols and that cyclohexanedi-methanol comprises greater than about 25 mole % of the total glycols.

The water dispersible polyesters and polyester-amides are, for the most part, water-dispersible because they form electrostatically-stabilized colloids when mixed with water. The colloid particle size varies with the polymer composition but has been shown by light diffraction studies and transmission electron microscopy to be mostly 200-800 Å in diameter. The aqueous colloid dispersions exhibit a minimum precipitation of solid material with time, in the temperature range of 0.1-99.9°C because the relationship between the particle densities and viscosities (very similar to those of water when concentrations are less than 30 weight percent) are such that thermal energy expressed as Brownian motion is sufficient to keep the particles suspended in water.

The water-dispersible polyesters have an inherent viscosity of at least 0.1 dL/g, preferably about 0.20-0.38 dL/g, when determined at 25°C using 0.25 g polymer per 100 ml of a solvent consisting of 60 parts

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by weight phenol and 40 parts by weight tetrachloroethane.

The sulfonate-containing, water-dispersible, linear polymers thus comprise polyesters, including polyester-amides, consisting of repeating, alternating residues of

5 (1) one or more dicarboxylic acids and (2) one or more diols or a combination of one or more diols and one or more diamines where, in the preceding definition, the mole percentages are based on 100 mole percent

10 dicarboxylic acid residues and 100 mole percent diol or diol and diamine residues. Alternatively, the polymers may include residues of monomers having mixed functionality such as hydroxycarboxylic acids, aminocarboxylic acids and/or aminoalkanols.

15 In the above latexes, the polyester or polyester-amide is preferably present in about 1 to 20 weight percent, based on the total weight of solids, more preferably 1 to 10 weight percent, and most preferably 1 to 6 weight percent.

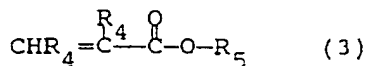
20 In the above latexes, ethylenically unsaturated species which can be utilized include, for example, acrylic monomers such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, isopropyl methacrylate, butyl

25 acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, octyl acrylate, hydroxyethyl methacrylate, alkenyl aromatic compounds (e.g., styrene, α -methyl styrene, vinyl naphthalene, and the like), vinyl

30 compounds (e.g., vinyl esters such as vinyl acetate, vinyl propionate, vinyl chloride, vinyl neodecanoate, and the like), multifunctional acrylate and multifunctional methacrylate compounds (e.g., trimethylolpropane triacrylate and the like), di-n-butyl

35 maleate, and compounds of the general formula (3)

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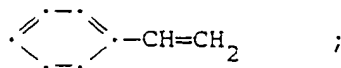
wherein R_4 is independently hydrogen or methyl and
 10 R_5 is $\text{C}_1\text{--C}_{12}$ alkyl;
 acetoacetoxyethyl methacrylate, acetoacetoxyethyl
 acrylate, acetoacetoxy(methyl)ethyl acrylate,
 acetoacetoxypropyl acrylate, and acetoacetoxybutyl
 acrylate. Such compounds provide a polymer with
 15 pendant acetoacetoxy groups which may optionally treated
 with ammonia or a primary or secondary amine to provide
 an enamine group as taught in EP 492 847.

Further ethylenically unsaturated compounds include
 t-butylaminoethyl methacrylate, N,N-dimethylaminoethyl
 20 methacrylate, N-dimethylaminopropyl methacrylamide, 2-t-
 butylaminoethyl methacrylate, and N,N-dimethylaminoethyl
 acrylate. Especially preferred compounds of Formula (2)
 include t-butylaminoethyl methacrylate and N,N-
 dimethylaminoethyl methacrylate.

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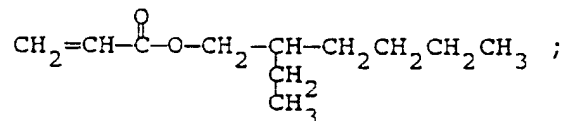
Preferred ethylenically unsaturated compounds
 include the following:

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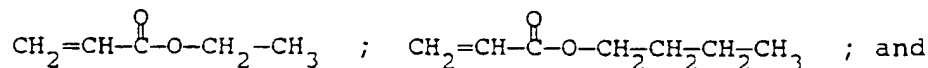
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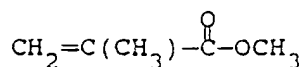
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In the above formulae, the alkyl and alkylene groups may be straight or branched chain.

The polymers may further be prepared from known wet adhesion-promoting monomers, including methacrylamido-
5 ethylethyleneurea and/or N-(2-methylacryloyloxyethyl)ethylene urea.

In the polymerization process, any number of free radical initiators (both thermal and redox systems) can be used to generate small particle size latexes. Typical
10 initiators include hydrogen peroxide, potassium or ammonium peroxydisulfate, dibenzoyl peroxide, lauryl peroxide, ditertiary butyl peroxide, 2,2'-azobisisobutyronitrile, t-butyl hydroperoxide, benzoyl peroxide, and the like.

15 Suitable reducing agents are those which increase the rate of polymerization and include for example, sodium bisulfite, sodium hydrosulfite, sodium formaldehyde sulfoxylate, ascorbic acid, isoascorbic acid, and mixtures thereof.

20 Suitable catalysts are those compounds which increase the rate of polymerization and which, in combination with the above described reducing agents, promote decomposition of the polymerization initiator under the reaction conditions.

25 Suitable catalysts include transition metal compounds such as, for example, ferrous sulfate heptahydrate, ferrous chloride, cupric sulfate, cupric chloride, cobalt acetate, cobaltous sulfate, and mixtures thereof.

30 However, due to the negative effect of added electrolyte on the stability of the water-dispersible polyesters used in this invention, it is necessary to minimize the electrolyte content of the latex recipe to minimize coagulum. For this reason, the preferred
35 initiator, as part of a redox pair, is t-butyl

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hydroperoxide (TBHP). The preferred reductants for redox system used in this invention are sodium formaldehyde sulfoxylate (SFS), isoascorbic acid (IASA) and ascorbic acid (AsA) with the most preferred
5 reductant being isoascorbic acid. Finally, though it is not necessary, chain transfer agents such as mercaptans may be used to control the molecular weights of the seed and/or any or all of the subsequent polymerization stages. Exemplary chain transfer agents are butyl
10 mercaptan, mercaptopropionic acid, 2-ethylhexyl 3-mercaptopropionate, n-butyl 3-mercaptopropionate, octyl mercaptan, isodecyl mercaptan, octadecyl mercaptan, mercaptoacetic acid, and the reactive chain transfer agents taught in U.S. Patent No. 5,247,040,
15 incorporated herein by reference, in particular, allyl mercaptopropionate, allyl mercaptoacetate, crotyl mercaptopropionate, and crotyl mercaptoacetate.

One process for preparing these polymers involves charging the water-dispersible polyester or polyester-
20 amide to a reactor, feeding in the monomers for the first stage of the latex under monomer starved conditions. As used herein, the term "starved-feed" or "monomer starved" refers to a process where a mixture of the monomers and separately the initiator are fed into
25 the preheated reaction mixture over a period of time. This process results in better compositional control of the copolymers since a high conversion of monomer to polymer is maintained in the reaction vessel. This process also results in better temperature control of
30 the polymerization. The addition rate and process temperature is optimized for the initiator used. The reaction is preferably conducted at about 65°C under an inert gas such as nitrogen, and the polymerization is initiated using a free radical redox initiator such as
35 t-butyl peroxide/isoascorbic acid. After the first

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stage monomers are fed into the reactor, a mixture of monomers, comprised of, for example, styrene, butyl acrylate, and the monomers of which define the second stage are fed into the reactor.

5 As a further aspect of the present invention there is provided a latex coating composition which comprises the polyester/acrylic hybrid latex polymers as described above, further comprising one or more leveling, rheology, and flow control agents such as silicones,
10 fluorocarbons or cellulosics; extenders; reactive coalescing aids such as those described in U.S. Patent No. 5,349,026, incorporated herein by reference; plasticizers; flattening agents; pigment wetting and dispersing agents and surfactants; ultraviolet (UV)
15 absorbers; UV light stabilizers; tinting pigments; extenders; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors;
20 thickening agents; or coalescing agents.

Specific examples of such additives can be found in Raw Materials Index, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D.C. 20005. Further examples of such
25 additives and emulsion polymerization methodology may be found in U.S. Patent No. 5,371,148, incorporated herein by reference.

Examples of flattening agents include synthetic silica, available from the Davison Chemical Division of
30 W.R. Grace & Company under the trademark SYLOID®; polypropylene, available from Hercules Inc., under the trademark HERCOFLAT®; synthetic silicate, available from J.M. Huber Corporation under the trademark ZEOLEX®.

Examples of dispersing agents and surfactants
35 include sodium bis(tridecyl) sulfosuccinnate, di(2-ethyl

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hexyl) sodium sulfosuccinnate, sodium dihexylsulfo-
succinnate, sodium dicyclohexyl sulfosuccinnate, diamyl
sodium sulfosuccinnate, sodium diisobutyl sulfo-
succinnate, disodium iso-decyl sulfosuccinnate, disodium
5 ethoxylated alcohol half ester of sulfosuccinnic acid,
disodium alkyl amido polyethoxy sulfosuccinnate, tetra-
sodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfo-
succinamate, disodium N-octasulfosuccinamate, sulfated
ethoxylated nonylphenol, 2-amino-2-methyl-1-propanol,
10 and the like.

Examples of viscosity, suspension, and flow control
agents include polyaminoamide phosphate, high molecular
weight carboxylic acid salts of polyamine amides, and
alkylene amine salts of an unsaturated fatty acid, all
15 available from BYK Chemie U.S.A. under the trademark
ANTI TERRA®. Further examples include polysiloxane
copolymers, polyacrylate solution, cellulose esters,
hydroxyethyl cellulose, hydrophobically-modified
hydroxyethyl cellulose, hydroxypropyl cellulose, poly-
20 amide wax, polyolefin wax, carboxymethyl cellulose,
ammonium polyacrylate, sodium polyacrylate, and poly-
ethylene oxide. Other examples of thickeners include
the methylene/ethylene oxide associative thickeners and
water soluble carboxylated thickeners, for example,
25 those sold under the UCAR POLYPHOBE trademark by
Union Carbide.

Several proprietary antifoaming agents are
commercially available, for example, under the trademark
BRUBREAK of Buckman Laboratories Inc., under the Byk®
30 tradename of BYK Chemie, U.S.A., under the Foamaster®
and Nopco® trademarks of Henkel Corp./Coating Chemicals,
under the DREWPLUS® trademarks of the Drew Industrial
Division of Ashland Chemical Company, under the TRYSOL®
and TROYKYD® trademarks of Troy Chemical Corporation,

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and under the SAG® trademarks of Union Carbide Corporation.

Examples of fungicides, mildewcides, and biocides include 4,4-dimethyloxazolidine, 3,4,4-trimethyl-
5 oxazolidine, modified barium metaborate, potassium N-hydroxy-methyl-N-methyldithiocarbamate, 2-(thiocyano-methylthio) benzothiazole, potassium dimethyl dithiocarbamate, adamantane, N-(trichloromethylthio) phthalimide, 2,4,5,6-tetrachloroisophthalonitrile,
10 orthophenyl phenol, 2,4,5-trichlorophenol, dehydroacetic acid, copper naphthenate, copper octoate, organic arsenic, tributyl tin oxide, zinc naphthenate, and copper 8-quinolate.

Examples of U.V. absorbers and U.V. light
15 stabilizers include substituted benzophenone, substituted benzotriazoles, hindered amines, and hindered benzoates, available from American Cyanamid Company under the trademark CYASORB UV, and diethyl-3-acetyl-4-hydroxy-benzyl-phosphonate, 4-dodecyloxy-2-
20 hydroxy benzophenone, and resorcinol monobenzoate.

As a further aspect of the present invention, there is provided a coating composition optionally containing one or more of the above-described additives. It may also be desirable to utilize a water-miscible organic
25 solvent and/or coalescing agent. Such solvents and coalescing agents are well known and include ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, ethylene glycol monobutyl ether, propylene glycol n-butyl ether, propylene glycol methyl ether,
30 propylene glycol monopropyl ether, dipropylene glycol methyl ether, diacetone alcohol, TEXANOL® ester alcohol (Eastman Chemical Company), and the like. Such solvents and coalescing aids may also include reactive solvents and coalescing aids such as diallyl phthalate, SANTOLINK
35 XI-100® polyglycidyl allyl ether from Monsanto, and

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others as described in U.S. Patent Nos. 5,349,026 and 5,371,148, incorporated herein by reference.

(See, for example, J. K. Backus in "High Polymers, Vol. 29, 1977, p. 642-680).

5 As a further aspect of the present invention, there is provided a coating composition as set forth above, further comprising one or more pigments and/or fillers in a concentration of about 1 to about 70 weight percent, preferably about 30 to about 60 weight percent,
10 based on the total weight of the solids in the composition.

 Pigments suitable for use in the coating compositions envisioned by the present invention are the typical organic and inorganic pigments, well-known to
15 one of ordinary skill in the art of surface coatings, especially those set forth by the Colour Index, 3d Ed., 2d Rev., 1982, published by the Society of Dyers and Colourists in association with the American Association of Textile Chemists and Colorists. Examples include,

20 but are not limited to the following: CI Pigment White 6 (titanium dioxide); CI Pigment Red 101 (red iron oxide); CI Pigment Yellow 42, CI Pigment Blue 15, 15:1, 15:2, 15:3, 15:4 (copper phthalocyanines); CI Pigment Red 49:1; and CI Pigment Red 57:1.

25 Upon formulation above, the coating compositions is then applied to the desired substrate or article, e.g., steel, aluminum, wood, gypsum board, or galvanized sheeting (either primed or unprimed), and allowed to air dry. Any coating composition designed for industrial
30 coatings, textile coatings, ink coatings, adhesives, or coatings for plastics are within the scope of the present invention and is included in the term "article". Thus, as a further aspect of the present invention, there is provided an article which has been coated with

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the coating compositions of the present invention and dried.

5 The latex compositions of the present invention may be used alone or in combination with other waterborne coating compositions in the form of a blend. Accordingly, as a further aspect of the invention, there is provided a waterborne coating composition comprising a blend of the hybrid latexes of the present invention and a water-dispersible polymer selected from the group
10 consisting of alkyds, polyesters, polyester-amides, cellulose esters, polyurethanes, polyethers, acrylics, and vinyl polymers.

Experimental Section

15

In the following examples dealing with polyester preparation, the amounts of acids used are expressed so that the total of the acids equals 100%; the amounts of the various glycols similarly totals 100%. All per-
20 centages are expressed as mole-percent.

Example I

This example illustrates the preparation of a
25 polyester containing 78% isophthalic acid, 22% 5-sodio-sulfoisophthalic acid, 10% ethylene glycol, and 90% 1,4-cyclohexanedimethanol (polyester 2, Table 1). Other polyesters were prepared similarly.

A mixture of 8.00 lb of isophthalic acid, 17.17 lb
30 of bis(2-hydroxyethyl) 5-sodiosulfoisophthalate as a 25 wt % solution in ethylene glycol (which contained titanium polyesterification catalyst sufficient to give final polymer containing ~100 ppm of Ti), 9.57 lb of 1,4-cyclohexanedimethanol, and 45 g of anhydrous sodium
35 acetate were charged to a 50 gal stainless steel reactor

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and heated under a nitrogen atmosphere to 200°C for 1 hr, then to 220°C for an additional 2 hr. The vacuum was applied and the mixture was heated to 285°C for approximately 2 hr. The vacuum was released and the
5 polymer extruded. It had I. V. (60/40 phenol/-tetrachloroethane) of 0.26.

Example II

10 This example illustrates the preparation of aqueous dispersions of one of the polyesters used in the process of this invention.

Deionized water (70 g) was heated to 90°C, stirred vigorously, and 30 g of the polymer of Example 1 was
15 added in 7.5 g increments, with a 15 min interval between additions. The dispersion was stirred for an additional 1 hr at 90°C, then cooled to room temperature and filtered through 2 layers of cheese cloth. The resulting clear, light yellow dispersion contained
20 31.35% solids; the pH was 5.7, and the viscosity was 42.1 cps (60 rpm, #2 spindle, Brookfield viscometer).

Example III

25 This example illustrates the preparation of the latex of Example 1 in Table I.

Latex Preparation I

30 Water (150 g), 14.35 g Polyester of Example I—dispersion (31.35% solids), .08 g sodium carbonate were placed in a 3-necked round bottom flask which was equipped with a mechanical stirrer, flushed with nitrogen, and heated to 50°C. The mixture was stirred,
35 and 1.0 g of a 1% solution of aluminum iron sulfate and

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a solution of 0.25 g of isoascorbic acid in 2 g of water was added. Controlled addition of catalyst and reactant solutions were then started as follows: 1 g tert-butyl peroxide in 25 g of water (1) (0.186 g/min); 0.5 g
5 isoascorbic acid in 25 g water (11) (0.186 g/min); and a mixture of 230.50 g of water, 1.35 g of TREM LF40 surfactant, 36.36 g of butyl acrylate; 6.0 g of hydroxyethyl methacrylate; 3.0 g of ethylene glycol dimethacrylate; 28.53 g of methyl methacrylate; 4.50 g
10 of sodium 2-acrylamido-2-methyl-propane sulfonate ("AMPS"), and 0.35 g of sodium carbonate (III), added at 4.426 g/min.

After the addition of solution III was complete, the addition of a solution of 2.25 g of TREM LF40
15 surfactant, 3.0 g of ethylene glycol dimethacrylate, 76.5 g of butyl methacrylate, 40.91 g of butyl acrylate, and 54.21 g of methyl methacrylate (solution IV) was started, at 4.426 g/min.

After the addition of solution IV was complete, the
20 ~~addition of a solution of 12.36 g of methyl~~
methacrylate, 13.50 g of butyl methacrylate, 13.63 g of butyl acrylate, 0.90 g of TREM LF40 surfactant, and 3.0 g of A-174 (crosslinker) was started at 4.426 g/min.

After addition of the final solution, the mixture
25 was cooled and filtered through 100 mesh wire screen. The resulting latex had pH of 7.3, % solids of 39.79, and NO scrap. (Table I, Ex. 2).

Example IV

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This example illustrates the preparation of the latex of Example 2 in Table I.

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Latex Preparation II

The procedure of Latex Preparation (Example III) was followed except that 14.86 g of polyester dispersion (30.29% solids) was added initially, and the water in solution III was 229.99 g. The polyester was 77% isophthalate, 23% 5-sodiosulfoisophthalate, 77% diethylene glycol, and 23% 1,4 cyclohexanedimethanol. The final latex had pH of 7.2, % solids of 38.17, and dry scrap of 18.5 g (Table 1, Ex. 3).

Example V

This example illustrates the preparation of another polyester stabilizer of the present invention.

Polymer II Preparation

Polymer of 78 mol % isophthalic acid, 22 mol % 5-sodiosulfoisophthalate, 80 mol % 1,4-cyclohexanedimethanol, and 20 mol % diethylene glycol — X-23657-162 (Lab Prep) 77.69 g (0.468 moles) of isophthalic acid (Amoco), 39.07 g (0.132 moles) of dimethyl 5-sodiosulfoisophthalic acid (Dupont), 72.58 g (0.504 moles) 1,4 cyclohexanedimethanol (Eastman), 25.44 g (0.24 moles) of diethylene glycol (Kodak), 1.08 g (0.0132 moles) of sodium acetate (Mallinckrodt), and 0.90 ml (~75 ppm Ti) of a Ti tetra-isopropyl titanate solution were placed in a 500-ml single-necked round bottom glass flask equipped with a stainless steel stirrer with paddle, N₂ inlet, take-off vessel, dry-ice traps. The flask and contents were placed under a N₂ purge and then inserted into a Belmont metal bath with a temperature controller. A Heller stirrer/motor assembly was used for agitation. The chemicals were reacted,

- 19 -

with stirring, at 200°C for 1 hour with removal of water/methanol; the temperature was increased to 220°C and the reaction product stirred an hour at this temperature with removal of additional water/methanol and other volatiles. The temperature was increased to 250°C and held for 30 minutes; a clear melt was obtained. The temperature was increased to 275°C and the system was placed under vacuum using an oil-based electrical pump. The reaction was stirred under a 0.2 mm vacuum for ~ 1 hour with removal of additional water/methanol and excess diethylene glycol. A clear, viscous, light yellow melt was obtained. The polymer was removed from the bath, cooled, and isolated. A polyester with an I.V. of 0.315, 2nd cycle Tg of 80°C, and composition by NMR of 77.6 mol % isophthalate, 22.4 mol % 5-sodiosulfoisophthalate, 77.6 mole % 1,4-cyclohexanedimethanol, and 22.4 mol % diethylene glycol was obtained. (The acid components are calculated to equal 100 mol % and the glycol components are calculated to equal 100 mole %).

Other polyester compositions can be prepared in a similar fashion either on a small scale in the lab, in the pilot plant batch or continuous equipment, or by scale-up to commercial scale in either batch or continuous units. The polymers may be prepared from the diacids, diesters, or anhydrides with Ti or other suitable known esterification, ester-exchange, and/or polycondensation catalysts.

30 Example VI

This example illustrates the preparation of a latex from the polymer of Example V (Example 3, Table I).

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- 20 -

Latex of Polymer II (Example V)

Water (150 g), aqueous polymer dispersion (16.88 g
5 of a 30.6% solids dispersion of polyester of Example V)
were placed in a 3-necked round bottom flask which was
equipped with a mechanical stirrer and flushed with
nitrogen. The mixture was stirred, and 1.0 g of a 1%
10 solution of ammonium iron sulfate and a solution of
0.25 g of isoascorbic acid in 2.0 g water was added.
Controlled addition of catalyst and reactant solutions
were then started as follows: 1 g t butyl hydroperoxide
in 30 g water (I) (0.182 g/min); 0.90 g isoascorbic acid
in 30 g water (II) (0.182 g/min); and a mixture of
15 182.79 g water, 0.40 g sodium carbonate, 175.50 g butyl
acrylate, 6.75 g hydroxyethyl methacrylate, 5.06 g
acrylic acid, 50.63 g styrene, 2.0 g Aerosol OT75,
1.69 g 2-ethyl hexyl mercaptopropionate, 37.97 g butyl
methacrylate (III) (3.454 g/min).

20 After the addition of solution III was complete,
~~the addition of a solution of 4.22 g butyl methacrylate,~~
43.88 g butyl acrylate, 0.50 g Aerosol OT75, 6.75 g
hydroxyethyl acrylate (IV) was started at 3.454 g/min.

After all the material was added, the material was
25 cooled and filtered through a 100 mesh wire screen. A
latex with pH 4.30, % solids of 45.4, and only a trace
of scrap was obtained. (Ex. 4, Table 1).

Comparative Example VII

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This example illustrates the preparation of a third
type of polyester stabilizer.

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Polymer Preparation III

Using the same procedure and set up as for Polymer Preparation II (Example V), 74.70 g (.45 Moles) of isophthalic acid, 44.40 g (.15 moles) of dimethyl 5-sodiosulfoisophthalate, 52.89 g (.33 moles, 10% excess) of 2-butyl, 2-ethyl 1,3 propanediol and 55.80 g (.9 moles, 200% excess) of ethylene glycol, 1.23 g (0.015 moles) of anhydrous sodium acetate and 0.83 ml (~75 ppm Ti) of a titanium tetraisopropyl titanate catalyst solution were stirred and heated at 200°C for 1 hour, the temperature was increased to 250°C and stirred an additional hour, the temperature was then increased to 275°C, the system was placed under a vacuum of <1.0 mm Hg and held for 40 minutes. A light brown polymer was obtained. I.V. (60/40 phenol/tetrachloroethane) was 0.157 and NMR composition was 74 moles isophthalate, 26 moles of 5-sodiosulfoisophthalate, 44.1 moles of 2-butyl, 2-ethyl, 1,3-propanediol, 54 moles ethylene glycol, and 1.9 moles diethylene glycol.

Example VIII

This example illustrates the preparation of latex from the stabilizer of Example VII.

Latex of Polymer III

Weights of materials used and the procedure were identical to that shown in Latex Preparation of Example VI above. The polymer composition is shown in Polymer Prep III (Example VII) above. The polyester dispersion contained 29.9% solids and had a pH of 6.17. The

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resulting latex had a pH of 4.70, % solids of 39.50, and a large amount of scrap. (Ex. 15, Table I).

The other polymers and lattices listed in Table I were prepared in the same manner as Examples V-VIII; the relative amounts of the final latex composition for these are listed at the bottom of the table.

Example IX

In addition to the examples listed above and in Table 1, lattices were prepared with 8.1 and 5.3% polyester stabilizer (with no added surfactant) with the polymer and dispersion of Polymer Preparation II (Example V) (High SIP). In addition, other polyesters evaluated were AQ-29 (89% isophthalate, 11% 5-sodiumsulfoisophthalate and 100% diethylene glycol); AQ-38 (89% isophthalate, 11% 5-sodiumsulfoisophthalate, 78% diethylene glycol, and 22% 1,4-cyclohexanedimethanol); AQ-55 (82% isophthalate, 18% 5-sodiumsulfoisophthalate, 54% diethylene glycol, and 46% 1,4-cyclohexanedimethanol); LB (89% isophthalate, 11% 5-sodiumsulfoisophthalate, 72 mole % diethylene glycol and 28 mole % ethylene glycol).

The equipment and reaction conditions used for this method are outlined below.

Preparation of Latex Emulsion

Equipment and Set-Up - Two jacketed reaction kettles with seals and a 3-necked reaction kettle cover were set up in series. A McCarter clamp and chain clamp were used to hold the kettle together and attached to the rack. Lightning Brand Laboratory II Mixers with stainless steel shaft and A100 impeller were used to

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stir the reaction medium. A circulating heating Haake water bath (Model 43303-11) was used as heating medium. A water-cooled condenser with Y-tube was used. One side neck was equipped with a N₂ purge and a septum cover
5 through which the lines for the initiators, reductants, monomers were inserted. FM Lab Pumps were used for the initiators/reductants and for monomers.

Reaction Conditions — Initial charge materials were weighed and transferred to the kettle. A slow
10 nitrogen purge was used during the reaction and the water bath was set to the desired temperature. The kettle was purged with N₂ at least 10 minutes before any kicker, initiators, or monomers were fed into the system. Kickers were fed into the system just before
15 the initiator and monomer feeds were started. Initiators/reductants and monomers were weighed into Erlenmeyer flasks, feed rates were calibrated, and then these materials were fed at specified rates into the reaction kettle. After all the material had been fed
20 into the kettle, the pumps were turned off and the system was stirred at the set temperature for 30-90 minutes, normally for 60 minutes. The contents of the reaction kettle were cooled with stirring to ~ room temperature by circulating cold water through the
25 jacket. The agitator was stopped and the latex was filtered through a preweighed wire mesh screen (100 mm) to capture any scrap. Scrap was also carefully removed from the agitator blades and shaft. The scrap was air dried for 24 hours and reweighed. Percent solids and
30 particle size were determined on the filtered latex.

The data for these two sets of experiments are shown in Tables 2 and 3. Calculations for % SO₃Na and [% SO₃Na + % O] for these polymers are shown in Table 4.

The unexpectedly superior performance of the class
35 of polymeric stabilizers disclosed in this invention

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report is apparent from examination of Table 1. Examples 1 and 3-8 of that table, in which the % 0 and % -SO₃Na fall within the prescribed limits; gave small amounts of coagulum, and the particle size of the latex was small. Example 2 gave a relatively large amount of coagulum; Example 10 gave a small amount of coagulum, but the latex had a very large particle size. Examples 9 and 11-16, in all of which one or both of the % 0 and % -SO₃Na are outside of the limits claimed in this invention, gave large amounts of coagulum and/or latex with large particle sizes.

In addition, the data in Tables 2, 3 and 4 show that the high SIP polymer is the only one of this series that meets the criteria and it showed superior results to the other polyester systems. These data also showed that at 5-8% polyester, low scrap levels could be obtained with no additional surfactant for the emulsion systems evaluated.

Table I

Polyester Composition

a Ex	b Acids (mol %)	c Glycols Form (mol %)	Repeat Unit Wt.	% SO ₃ Na	% O	SO ₃ Na + O	% Solid	Particle Size	Coagulum
1	1 (78), SIP (22)	CHDM (90), EG (10)	288.3	7.86	22.20	30.46	39.79		Clean
2	1 (77), SIP (23)	DEG (77), CHDM (23)	268.2	8.83	28.45	37.28	38.17		18.5 g
3	1 (77.6); SIP (22.4)	CHDM (77.6), DEG (22.4)	288.3	8.00	23.44	31.44	45.40	69	Trace
4	CHDA (78), SIP (22)	CHDM (78), DEG (22)	292.8	7.74	23.06	30.80	44.60	72	Trace
5	1 (78), SIP (22)	CHDM (80), DEG (20)	288.8	7.84	23.27	31.12	45.00	74	Small Amt.
6	1 (38.7), T (39.3) SIP (22)	CHDM (77.5), DEG (22.5)	267.9	7.87	23.48	31.35	44.60	68	1.1 g
7	CHDA (78), SIP (22)	CHDM (75), DEG (25)	291.6	7.77	23.32	31.09	45.10	73	2.4 g
8	1 (77), SIP (23)	BEPD (68), DEG (32)	296.2	7.99	23.34	31.33	44.70	111	5.5 g

Table I (Cont'd.)

<u>Polyester Composition</u>			<u>Repeat Unit Form Wt.</u>	<u>% SO₃Na</u>			<u>% SO₃Na + O</u>			<u>Particle Size</u>		<u>Coagulum</u>
<u>Ex.</u>	<u>a</u> <u>Acids</u> <u>(mol %)</u>	<u>b</u> <u>Glycols</u> <u>(mol %)</u>		<u>% SO₃Na</u>	<u>% O</u>	<u>% Solid</u>	<u>% SO₃Na + O</u>	<u>% Solid</u>	<u>% Solid</u>	<u>Size</u>	<u>Coagulum</u>	
9	1 (76), SIP (24)	BEPD (42), DEG (58)	283.2	8.73	25.88	34.51	45.20	971	Small Amt.			
10	1 (85), SIP (15)	CHDM (75), DEG (25)	279.8	5.52	24.30	29.82	43.70	131	14.4			
11	CHDA (77), SIP (23)	NPG (100)	262.1	9.04	24.42	33.46			Bad			
12	1 (65), SIP (15)	BEPD (68), DEG (32)	288.0	5.36	24.00	29.36	40.60	113	Large Amt.			
13	CHDA (77), SIP (23)	CHDM (67), DEG (33)	289.5	8.18	23.93	32.11	37.30	81	Large Amt.			
14	1 (74), SIP (26)	BEPD (48), EG (54)	263.6	10.16	24.28	34.44	39.50	69	Large Amt.			
15	1 (78), SIP (22)	BEPD (19), DEG (21)	268.7	8.43	26.64	37.07	—	—	Unstable			

Table I. (Cont'd.)

<u>Polyester Composition</u>			<u>Repeat Unit Form Wt.</u>				<u>Particle Size</u>	<u>Coagulum</u>
<u>Ex</u>	<u>a</u> <u>Acids</u> <u>(mol %)</u>	<u>b</u> <u>Glycols</u> <u>(mol %)</u>		<u>% SO₃Na</u>	<u>% O</u>	<u>SO₃Na + O</u>		
16	1 (84) SIP (13)	BEPD (75); DEG (25)	292.8	5.63	23.22	28.85	18.20	203
								No Conv.

NOTES

a. In Ex. 1 & 2, the components are those shown in Latex Examples I and III. In Ex. 3-16, all emulsions were prepared to a theoretical 45% solids level at 1.5% polyester stabilizer, 2.5 g Aerosol OT surfactant, 0.40 g ammonium carbonate and the following vinyl/acrylic monomers; 65 g butyl acrylate, 15 g styrene, 12.5 g butyl methacrylate, 2 g hydroxyethyl methacrylate, 20 g hydroxyethyl acrylate, 0.50 g ethylhexyl mercaptopropionate, and 1.5 g acrylic acid. The monomer weights were based upon a total of 100 g of monomers (acrylic/vinyl + AQ polyester).

b. Acid Abbreviation: 1, Isophthalic Acid; SIP, 5-sodiosulfisophthalic Acid; CHDA, 1,4-cyclohexanedicarboxylic Acid; T, Terephthalic Acid.

c. Glycol Abbreviations: CHDM, 1,4-cyclohexanedimethanol; DEG, Diethylene Glycol; BEPD, 2-butyl-2-ethyl-1,3 propanediol; NPG, 2,2-dimethyl-1,3-propanediol; EG, ethylene glycol.

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Experiment 1 - 8.11% Polyester, t-butyl hydroperoxide/
ammonium iron sulfate/isoascorbic acid
initiator/reductant system

5 The first set of experiments (as shown in table 2
below) used the following conditions: 8.11% polyester
(390.70 g demineralized H₂O, 69.95 g polyester
dispersion - except for AQ-55 which used 397.03 g H₂O
10 and 63.32 g polyester dispersion) were placed in the
kettle under a N₂ purge and heated to 50°C. A kicker of
.550 g of a 1% ammonium iron sulfate solution, 0.30 g of
a 1% EDTA solution, and 0.1 g isoascorbic acid in 5 g
H₂O, and 0.10 g t-butylhydroperoxide in 5.0 g H₂O was
15 added. The initiator feed was 0.576 g t-butyl
hydroperoxide and 0.387 g ammonium carbonate in 35.0 g
demineralized H₂O (feed rate of 0.288 g/min) and the
reductant was 0.570 g isoascorbic acid in 35 g
demineralized H₂O (feed rate of 0.285 g/min). A 75/25
20 styrene/methylmethacrylate monomer solution (194.33 g
styrene/64.78 g MMA) was fed at 2.16 g/min. The
experiment was repeated with 25/75
styrene/methylmethacrylate monomer solution (64.78 g
styrene/194.33 g MMA). The total batch size was 800 g
25 and the theoretical % solids was 35%.

Table 2

<u>Polyester Source</u>	<u>Monomer</u>	<u>Ratio</u>	<u>% Solids</u>	<u>G Scrap</u>	<u>% Scrap</u>	<u>Part. Size</u>
AQ-29	Sty/MMA	75/25	32.27	0.828	.32	79
"	"	25/75	34.80	1.275	.49	77
"	"	"	34.83	1.698	.66	75
AQ-38	Sty/MMA	75/25	35.14	1.613	.62	83
"	"	25/75	84.83	1.545	.60	79
LB	Sty/MMA	75/25	34.55	5.771	2.23	82
"	"	25/75	34.22	1.221	.47	73
AQ-55	Sty/MMA	75-25	35.15	2.537	.98	59
"	"	"	35.03	1.548	.60	56
"	"	25/75	35.10	4.154	1.60	103
"	"	"	34.86	2.195	.85	59
High SIP	Sty/MMA	75-25	35.07	0.421	.16	58
"	"	25/75	35.18	0.588	.23	63

%Scrap is based on the g scrap/g theoretical monomer X100.

Particle Size is in nm and was measured on a Brookhaven BI-90.

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Table 3 shows the results for Experiment 2 which used an initiator/reductant system of ammonium persulfate/sodium bisulfite at 75/25 styrene/-methylmethacrylate and a polyester concentration of 5.26%.

Experiment 2 - 5.26% polyester, ammonium persulfate/-sodium bisulfite initiator/reductant system

5 A second set of experiments used the following conditions: 5.26% polyester (376.53 g demineralized H₂O, 43.60 g polyester dispersion - except for AQ-55 which used 380.49 g H₂O and 39.64 g dispersion); kicker
10 added was 0.45 g of 1% ammonium iron sulfate solution; the initiator was 0.453 g ammonium persulfate in 40.0 g demineralized H₂O at 0.270 g/min; reductant was 0.264 g/min; monomer was a 75/25 styrene/MMA solution (187.06 g/62.35 g) at a feed rate of 1.66 g/min. In
15 some instances ammonium carbonate (0.218 g) was added with the initiator. The total batch size was 750 g and the theoretical % solids was 35%. The temperature was 55°C.

Table 3

<u>Polyester Source</u>	<u>Ammonium Carbonate</u>	<u>% Solids</u>	<u>G Scrap</u>	<u>% Scrap</u>	<u>Part. Size</u>
AQ-29	No	34.2	1.931	71	71
"	Yes	-----	crashed	-100	-
AQ-55	No	34.3	1.000	.88	63
"	Yes	84.12	4.966	1.89	75
High SIP	No	34.83	0.413	.17	75
"	Yes	33.99	0.366	.15	69

% Scrap is based on the g scrap/g theoretical monomer X100.

Particle Size is in nm and was measured on a Brookhaven BI-90.

Table 4

<u>Polymer</u>	<u>Repeat Unit</u>	<u>% SO₃Na</u>	<u>% O⁽¹⁾</u>	<u>(% SO₃Na + % O)</u>
AQ-29	247.22	4.58	32.36	36.94
AQ-38	255.64	4.53	29.95	34.48
LB	232.82	4.82	32.15	36.97
AQ-55	271.84	6.82	26.72	33.54
High SIP	288.84	7.84	23.27	31.11

a) Calculations for % O omit the oxygen in SO₃Na

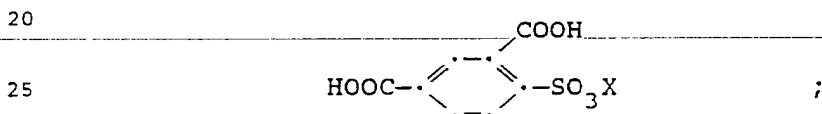
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Claims

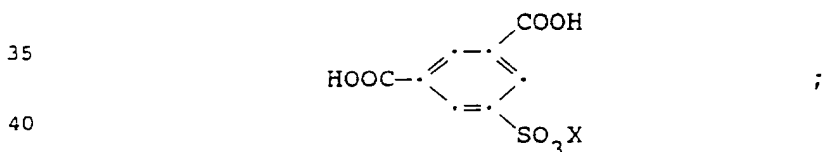
We Claim:

5 1. A polyester/acrylic hybrid latex having a particle size diameter of less than 100nm, prepared by the emulsion polymerization of ethylenically unsaturated monomers in the presence of a polyester stabilizer, wherein said polyester stabilizer is a water-dispersible
10 polyester is comprised of:

- (i) monomer residues of at least one aromatic or aliphatic dicarboxylic acid;
- 15 (ii) monomer residues of at least one difunctional sulfo monomer selected from the group consisting of



30 and



45 wherein X is Na⁺, K⁺, or Li⁺;

- (iii) monomer residues of at least one diol or a mixture of a diol and a diamine, wherein said
50 diol is selected from the group consisting of aliphatic and cycloaliphatic glycols; and optionally:

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- (iv) monomer residues of at least one difunctional monomer reactant selected from hydroxycarboxylic acids, aminocarboxylic acids and aminoalkanols;

5

wherein the weight percent of $-\text{SO}_3\text{X}$ groups is 7 to 8%, and the sum of the weight percent of $-\text{SO}_3\text{X}$ groups and oxygen, excluding the oxygen in said $-\text{SO}_3\text{X}$ groups, in said polyester is 30 to 32%.

10

2. The hybrid latex of claim 1, wherein the weight percentage of $-\text{SO}_3\text{X}$ groups in the water-dispersible polyesters is between 7.5 and 8 and the aromatic diacids are selected from the group consisting of terephthalic acid, isophthalic acid, and phthalic acid.

15

3. The hybrid latex of claim 1, wherein the aliphatic diacids are those having the general formula $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, wherein n is an integer of from 1 to 12, or are selected from the group consisting of 1,2-, 1,3-, and 1,4-cyclohexanedicarboxylic acid, maleic acid, fumaric acid, and 5(6)carboxy-4-hexyl-2-cyclohexene-1-octanoic acid.

20

25

4. The hybrid latex of claim 1, wherein the combination of aromatic diacids and difunctional sulfomonomers comprise 50 to 100 mole percent of the total dicarboxylic acid moieties and wherein the glycol residues are comprised of residues of one or more ethylene, diethylene, triethylene, tetraethylene, propylene, and dipropylene glycols and cyclohexanedimethanol.

30

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- 35 -

5. The hybrid latex of claim 4, wherein ethylene glycol comprises less than 75 mole % of the total glycols and that cyclohexanedimethanol comprises greater than 25 mole % of the total glycols.

5

6. The hybrid latex of claim 1, wherein the water-dispersible polyester is present in 1 to 10 weight percent, based on the total weight of solids.

10

7. The hybrid latex of claim 1, wherein the water-dispersible polyester is present in 1 weight percent to 6 weight percent, based on the total weight of solids.

15

8. The hybrid latex of claim 1, wherein the ethylenically unsaturated monomers are selected from the group consisting of acrylic monomers, alkenyl aromatic compounds, vinyl esters, multifunctional acrylate and multifunctional methacrylate monomers, compounds of the general formula

20



30

wherein R_4 is independently hydrogen or methyl and R_5 is C_1 - C_{12} alkyl; and

acetoacetoxo functional monomers.

35

9. A water-dispersible polyester comprised of:

- (i) monomer residues of at least one aromatic or aliphatic dicarboxylic acid;

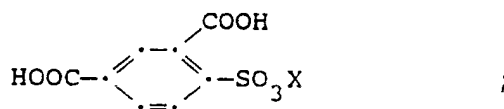
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- (ii) monomer residues of at least one difunctional sulfo monomer selected from the group consisting of

5

10

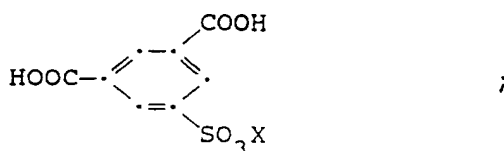


15

and

20

25



30

wherein X is Na⁺, K⁺, or Li⁺;

35

- (iii) monomer residues of at least one diol or a mixture of a diol and a diamine, wherein said diol is selected from the group consisting of aliphatic and cycloaliphatic glycols; and optionally:

40

- (iv) monomer residues of at least one difunctional monomer reactant selected from hydroxycarboxylic acids, aminocarboxylic acids and aminoalkanols;

45

wherein the weight percent of -SO₃X groups is 7 to 8%, and the sum of the weight percent of -SO₃X groups and oxygen, excluding the oxygen in said -SO₃X groups, in said polyester is 30 to 32%.

50

10. The water-dispersible polyester of claim 9, wherein the weight percentage of -SO₃X groups in the water-dispersible polyesters is between 7.5 and 8 and wherein the aromatic diacids are selected from the group

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consisting of terephthalic acid, isophthalic acid, and phthalic acid.

11. The water-dispersible polyester of claim 9,
5 wherein the aliphatic diacids are those having the
general formula $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, wherein n is an
integer of from 1 to 12, or are selected from the group
consisting of 1,2-, 1,3-, and 1,4-
cyclohexanedicarboxylic acid, maleic acid, fumaric acid,
10 and 5(6)carboxy-4-hexyl-2-cyclohexene-1-octanoic acid.

12. The water-dispersible polyester of claim 9,
wherein the combination of aromatic diacids and
difunctional sulfomonomers comprise 50 to 100 mole
15 percent of the total dicarboxylic acid moieties and
wherein the glycol residues are comprised of residues of
one or more ethylene, diethylene, triethylene,
tetraethylene, propylene, and dipropylene glycols and
cyclohexanedimethanol.

20

13. The water-dispersible polyester of claim 10,
wherein ethylene glycol comprises less than 75 mole % of
the total glycols and that cyclohexanedimethanol
comprises greater than 25 mole % of the total glycols.

25

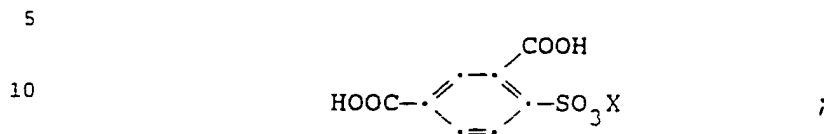
14. A waterborne coating composition comprising a
blend of a polyester/acrylic hybrid latex having a
particle size diameter of less than 100nm, prepared by
the emulsion polymerization of ethylenically unsaturated
30 monomers in the presence of a polyester stabilizer,
wherein said polyester stabilizer is a water-dispersible
polyester is comprised of:

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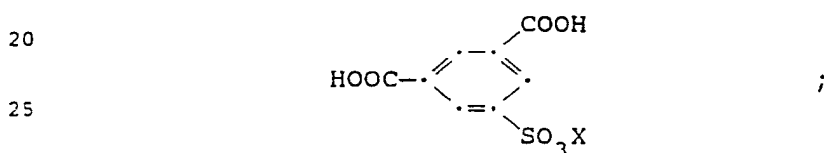
- (i) monomer residues of at least one aromatic or
aliphatic dicarboxylic acid;

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- (ii) monomer residues of at least one difunctional sulfo monomer selected from the group consisting of



15 and



30 wherein X is Na⁺, K⁺, or Li⁺;

- (iii) monomer residues of at least one diol or a mixture of a diol and a diamine, wherein said diol is selected from the group consisting of aliphatic and cycloaliphatic glycols; and optionally:

- (iv) monomer residues of at least one difunctional monomer reactant selected from hydroxycarboxylic acids, aminocarboxylic acids and aminoalkanols;

wherein the weight percent of -SO₃X groups is 7 to 8%, and the sum of the weight percent of -SO₃X groups and oxygen, excluding the oxygen in said -SO₃X groups, in said polyester is 30 to 32%; and

a water-dispersible polymer selected from the group consisting of alkyds, polyesters, polyester-amides, cellulose esters, polyurethanes, polyethers, acrylics, and vinyl polymers.

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15. A shaped or formed article coated with the
hybrid latex of claim 1.

16. A shaped or formed article coated with the
5 hybrid latex of claim 14.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/00912

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 283/02, C08G 69/44, C08G 63/688, C09D 151/08
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5342877 A (MARK D. CLARK), 30 August 1994 (30.08.94), claim 1, abstract --	1-16
A	WO 9505413 A1 (EASTMAN CHEMICAL COMPANY), 23 February 1995 (23.02.95), claims 1 and 24, abstract --	1-16
A	WO 9501382 A1 (EASTMAN CHEMICAL COMPANY), 12 January 1995 (12.01.95), claims 1 and 35, abstract --	1-16

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

7 May 1997

Date of mailing of the international search report

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Name and mailing address of the ISA/



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+ 31-70) 340-3016

Authorized officer

BARBRO NILSSON

International application No.

PCT/US 97/00912

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/04/97

International application No.

PCT/US 97/00912

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WO 9505413 A1	23/02/95	CA 2169299 A EP 0713503 A JP 9501712 T	23/02/95 29/05/96 18/02/97
WO 9501382 A1	12/01/95	NONE	
WO 9108237 A1	13/06/91	DE 3939918 A EP 0502879 A JP 5502250 T US 5277978 A	06/06/91 16/09/92 22/04/93 11/01/94